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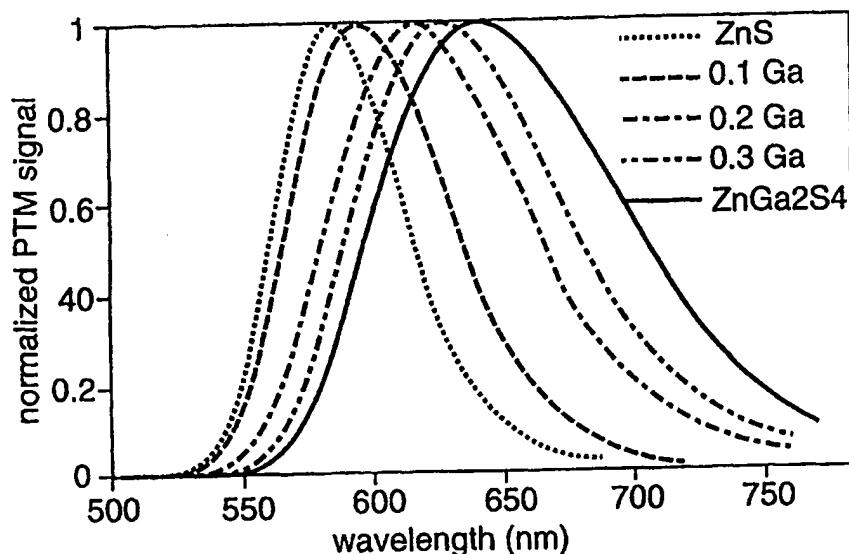
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| (71) Applicant (for all designated States except US): THE STATE OF OREGON acting by and through THE STATE BOARD OF HIGHER EDUCATION on behalf of OREGON STATE UNIVERSITY [US/US]; Corvallis, OR 97331-2140 (US). | | | |
| (72) Inventors; and | | Published | |
| (75) Inventors/Applicants (for US only): KESZLER, Douglas [US/US]; 8927 N.W. Lorri Pl., Corvallis, OR 97330 (US). LI, Dong [CN/US]; Apartment A1, 31 Golfview Drive, Newark, DE 19702 (US). WAGER, John, F. [US/US]; 2021 N.W. Woodland, Corvallis, OR 97330 (US). CLARK, Benjamin, L. [US/US]; 1607 S.W. 49th St., #16, Corvallis, OR 97333 (US). KEIR, Paul [US/US]; 3710 S.E. Stark, #12, Portland, OR 97214 (US). | | With international search report. | |
| (74) Agent: POLLEY, Richard, J.; Klarquist, Sparkman, Campbell, Leigh & Whinston, LLP, One World Trade Center, Suite 1600, 121 SW Salmon Street, Portland, OR 97204 (US). | | | |

(54) Title: PHOSPHOR SYSTEM



(57) Abstract

Phosphor compositions of the formula $Zn_{1-3x/2}M_xX:Mn$, wherein M is selected from the group consisting of the trivalent cations of Al, In, Ga, and mixtures thereof, and X is selected from the group consisting of S, Se, Te, and mixtures thereof are disclosed. Also disclosed are phosphor compositions of the formula, $MX:Cu, L, A$ wherein M is selected from the divalent ions of Sr, Mg, Ca, Ba, X is selected from the group consisting of S, Se, Te, and mixtures thereof, L is selected from the group consisting of the trivalent cations of the lanthanides, Al, In, Ga, Sc, and mixtures thereof, and A is selected from the alkali metal ions or mixtures thereof. Emission chromaticity of the phosphors is controlled by varying codopant concentrations. Electroluminescent devices comprising the phosphors are also disclosed.

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- 1 -

PHOSPHOR SYSTEM

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TECHNICAL FIELD

This invention relates to electroluminescent phosphor compositions that may be used for AC Thin Film Electroluminescent (ACTFEL) devices. This invention also relates to a crystal engineering method that allows chromatic control of phosphor emission across the visible spectrum. The invention further relates to luminescent devices produced from such phosphor compositions.

15

BACKGROUND OF THE INVENTION

Commercial electroluminescent (EL) devices are desirable for their wide viewing angles, crisp resolution, high contrast ratios, and durability. However, monochrome output and the unavailability of a suitable red-green-blue phosphor set have hampered widespread utility of electroluminescent devices.

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At present, commercial flat-panel EL devices operate on the basis of the amber emission from thin films of the phosphor ZnS:Mn. In order to realize full color output, suitable phosphors broadly emitting in the blue and yellow portions of the spectrum can be combined to produce a solid-state EL source of white light. The white emission from such phosphor combinations is then passed through appropriate color shutters. The drawback to this technique is that the light is greatly attenuated by passage through such shutters. In order to replicate the performance of a cathode-ray tube, it would be advantageous to provide efficient EL-active red, green, and blue phosphors having specific chromaticity values.

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SUMMARY OF THE INVENTION

The phosphor compositions described herein provide efficient,
5 electroluminescently active phosphors that may be used to provide a phosphor set that is substantially red, green, blue.

The crystal engineering methods of the invention provide chromaticity control that may be used to provide a highly efficient red, green, and blue phosphor set for electroluminescence applications.

10 A phosphor material is of the formula $Zn_{1-3x/2}M_xX:Mn$, wherein M is selected from the group consisting of the trivalent cations of Al, In, Ga, and mixtures thereof, and X is selected from the group consisting of S, Se, Te, and mixtures thereof. Most advantageously X is sulfur. The phosphor material exhibits a systematic red shift of its emission as x varies from 0.01 to 0.49. The
15 amount of Mn can be between 0.5 to 5.0 mol%, but control of the emission maximum is achieved by changing the amount of trivalent cation. The phosphor material can be used in a variety of electroluminescent devices.

Another phosphor material is of the formula $MX:Cu, L, A$ wherein M is selected from the divalent ions of Sr, Mg, Ca, Ba, and mixtures thereof, X is
20 selected from the group consisting of S, Se, Te, and mixtures thereof, L is selected from the group consisting of the trivalent cations of the lanthanides, Al, In, Ga, Sc, and mixtures thereof, and A is selected from the group consisting of the alkali metal ions and mixtures thereof. Most advantageously, X is sulfur and L is selected from the group consisting of the trivalent lanthanide cations and
25 mixtures thereof. This phosphor material undergoes a systematic blue shift in its emission maximum as the amount of L is increased from 0.05 to 5 mol% and undergoes a systematic red shift as the amount of A is increased from 0.05 to 5 mol%. The amount of copper can vary from 0.05 to 5.0 mol% copper, but need not be changed in order to vary the emission maximum. In a particular
30 embodiment the combined amount of L and A is equal to the amount of copper. This phosphor material can also be used in luminescent devices.

- 3 -

Advantageously a luminescent device includes both a phosphor material of the formula $Zn_{1-3x/2}M_xX:Mn$ and a phosphor material of the formula $MX:Cu, L, A$.

5 A luminescent device can be made by providing a suitable substrate and applying to the substrate at least one phosphor material selected from the group consisting of phosphor materials of the formula $Zn_{1-3x/2}M_xX:Mn$ and phosphor materials of the formula, $MX:Cu, L, A$.

BRIEF DESCRIPTION OF THE DRAWINGS

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FIG. 1 shows the photoemission spectra for a series of $Zn_{1-3x/2}Ga_xX:Mn$ phosphors where the Mn concentration is held at 1 at% and x is varied in the range $0 \leq x \leq 0.5$. Actual concentrations of Ga are as shown.

15 FIG. 2 shows the photoemission spectra for $SrS:Cu$ codoped with Na and Y where the Cu concentration is held at 0.2 at%. Concentrations of Na and Y are as shown.

FIG. 3 presents normalized electroluminescence spectra for a coactivated $SrS:Cu,Na,F$ (green) and a non-coactivated $SrS:Cu,F$ (blue) ACTFEL device.

20 FIG. 4 shows the Luminance-voltage (L-V) curves at 60 Hz for a coactivated $SrS:Cu,Na,F$ (green) and a non-coactivated $SrS:Cu,F$ (blue) ACTFEL device.

FIG. 5 shows the Efficiency-voltage (E-V) curves at 60 Hz for a coactivated $SrS:Cu,Na,F$ (green) and a non-coactivated $SrS:Cu,F$ (blue) ACTFEL device.

25 FIG. 6 shows the internal charge-phosphor field ($Q-F_p$) curves at 60 Hz and an overvoltage of 40V above threshold, for a coactivated $SrS:Cu,Na,F$ (green) and a non-coactivated $SrS:Cu,F$ (blue) ACTFEL device.

DETAILED DESCRIPTION

ZnMX:Mn Phosphor Systems

5 A phosphor material, useful in luminescent devices, is of the formula $Zn_{1-3x/2}M_xX:Mn$, wherein M is selected from the group consisting of the trivalent cations of Al, In, Ga, and mixtures thereof, and X is selected from the group consisting of S, Se, Te, and mixtures thereof. Most advantageously X is sulfur. The phosphor material exhibits a systematic red shift of its emission as x varies from 0.01 to 0.49.

10 The amount of Mn can be between 0.5 to 5.0 mol%, but control of the emission maximum is achieved by changing the amount of trivalent cation.

 A consideration of the electronic energy levels of the d^5 cation, Mn^{2+} , reveals that an increase in the crystal field strength will lead to a decrease in the separation of the energy levels and a red shift in its emission. An increase in the
15 crystal field strength may be effectuated by substituting Zn^{2+} ions with more highly charged trivalent cations, for example Al^{3+} or Ga^{3+} . Such substitutions yield cation vacancies within the crystal lattice. To maintain charge compensation on substitution, Zn defects will be formed, thereby lowering the coordination of some sulfur atoms. Such sulfur atoms will bond more strongly to Mn^{2+} ions in
20 comparison to those sulfur atoms not associated with a Zn vacancy. The increased binding strength leads to a stronger crystal field and a red shift in the emission from the Mn^{2+} ions. The method also includes monitoring the luminescence of phosphors made in accordance with the crystal engineering approach to select compositions with the desired chromaticity.

25 As shown in FIG. 1, the emission wavelength of the $ZnS:Mn$ phosphor can be specifically controlled in the system $Zn_{1-3x/2}Ga_xS:Mn$, i.e., a systematic wavelength shift was observed with increasing Ga concentration. Powder samples prepared at 1123K according to flux methods known in the art, revealed a decrease in the volume of the hexagonal cell of ZnS from 79.5 \AA^3 ($x=0$) to 77 \AA^3
30 ($x=.35$) as Ga^{3+} ions were introduced. Luminescent decay times and chromaticity values for a series of Ga substituted ZnS:Mn phosphors are shown below in table

- 5 -

1. The decay times were adequately fit by single-exponential functions and the lifetimes derived therefrom were consistent with direct emission from Mn centers. The composition $\text{Zn}_{0.55}\text{Ga}_{0.3}\text{S}:\text{Mn}$ yielded a true red phosphor as evidenced by its chromaticity values of $x = 0.64$ and $y = 0.36$. A similar red shift in emission upon substitution of Zn^{2+} with Al^{3+} has been observed. The luminescent lifetimes and chromaticity values for the $\text{Zn}_{1-3x/2}\text{Ga}_x\text{S}: 1 \text{ at \% Mn}$ phosphors are summarized in Table 1.

TABLE 1

Luminescent lifetimes and chromaticity values for $\text{Zn}_{1-3x/2}\text{Ga}_x\text{S}: 1 \text{ at \% Mn}$.

| | X | lifetime | Chromaticity (x,y) |
|---|-----|----------|--------------------|
| ZnS | 0 | 0.85ms | 0.54, 0.46 |
| $\text{Zn}_{0.85}\text{Ga}_{0.1}\text{S}$ | 0.1 | 0.75ms | 0.58, 0.43 |
| $\text{Zn}_{0.7}\text{Ga}_{0.2}\text{S}$ | 0.2 | 0.83ms | 0.62, 0.38 |
| $\text{Zn}_{0.55}\text{Ga}_{0.3}\text{S}$ | 0.3 | 0.75ms | 0.64, 0.36 |

MX:Cu, L, A Phosphor Systems

- Another phosphor material, useful in luminescent devices, is of the formula $\text{MX}:\text{Cu}, \text{L}, \text{A}$ wherein M is selected from the divalent ions of Sr, Mg, Ca, Ba, and mixtures thereof, X is selected from the group consisting of S, Se, Te, and mixtures thereof, L is selected from the group consisting of the trivalent cations of the lanthanides, Al, In, Ga, Sc, and mixtures thereof, and A is selected from the group consisting of the alkali metal ions and mixtures thereof. Most advantageously, X is sulfur and L is selected from the group consisting of the trivalent lanthanide cations and mixtures thereof. This phosphor material undergoes a systematic blue shift in its emission maximum as the amount of L is increased from 0.05 to 5 mol% and undergoes a systematic red shift as the amount of A is increased from 0.05 to 5 mol%. The amount of copper can vary from 0.05 to 5.0 mol% copper, but need not be changed in order to vary the emission

- 6 -

maximum. In a particular embodiment the combined amount of L and A is equal to the amount of copper.

Chromatic control in the SrS:Cu system was achieved by altering the coordination number of the Cu ions. Because the copper ions enter the lattice in the +1 oxidation state, Cu doping results in the formation of sulfur vacancies. The presence of sulfur vacancies results in two types of Cu sites; one without an adjacent sulfur vacancy (six-coordinate Cu) and one with an adjacent S vacancy (five-coordinate Cu). Rather than creating sulfur vacancies by increasing the copper concentration, it was discovered that monovalent and trivalent codopants could be used to increase or decrease the number of sulfur vacancies, respectively.

In accordance with this discovery, SrS:Cu powder phosphors exhibiting controlled emission wavelengths spanning the blue and green regions of the spectrum were prepared (FIG. 2). In contrast to prior art phosphor compositions, these colors were achieved by fixing the Cu^+ concentration, for example at 0.2 at%, and carefully adjusting the concentrations of the monovalent and trivalent codopants. Other copper concentrations may be used. Charge compensation of Cu^+ by incorporation of a trivalent cation, such as Y^{3+} for example, into the NaCl-type host lattice of SrS preserves a six-coordinate environment for the Cu^+ , leading to a predominant blue emission. Incorporation of a sufficient quantity of monovalent cations, such as Na^+ or other alkali-metal cations for example, leads to an increased formation of sulfur vacancies and a green emission. By varying the relative concentrations of the monovalent and trivalent codopants the concentration for the two types of emission centers and the resulting emission color can be controlled. The method also includes monitoring the luminescence of phosphors made in accordance with the crystal engineering approach to select compositions with the desired chromaticity.

Devices

Light emitting phosphor materials according to the present invention can be used in a variety of electroluminescent display devices. In particular the phosphor materials can be used in ACTFEL devices of the type described in U.S. Patent

- 7 -

No. 5,939,825, incorporated herein by reference. Such ACTFEL devices have front and rear electrode sets, a pair of insulators between the front and rear electrode sets. A thin film electroluminescent laminar stack, which includes a body of phosphor material in a layer, is provided between the insulators.

5 To provide such a device, a SrS:Cu,F thin-film phosphor layer with a thickness of 800-1000 nm was deposited onto a glass substrate coated with layers of indium tin oxide and aluminum-titanium oxide, which serve as the bottom transparent contact and the bottom insulator, respectively of the ACTFEL devices. The SrS:Cu,F deposition was accomplished by electron-beam evaporation of SrS
10 and simultaneous thermal co-evaporation of CuF₂. Next, a thin layer of the appropriate alkali-metal fluoride coactivator, for example LiF, NaF, KF, RbF, or CsF, was deposited by thermal evaporation. Subsequently, rapid thermal annealing of the layers was performed at about 800 °C for about 2 minutes. Finally, a top insulating layer of silicon oxynitride was deposited by plasma-
15 enhanced chemical vapor deposition, and aluminum dots were thermally evaporated as the top contact.

FIG. 3 shows a comparison of the EL spectra of a coactivated SrS:Cu,Na,F device of the invention and a non-coactivated SrS:Cu,F ACTFEL device. Note the dramatic red shift of the coactivated devices into the green
20 portion of the spectrum. The Commission Internationale de l'Eclairage (CIE) color coordinates (chromaticity) for the sodium fluoride coactivated device are CIE_x = 0.317 and CIE_y = 0.585, which are very close to that desired for an ideal green phosphor (i.e. CIE_x = 0.30, CIE_y = 0.60). The chromaticity values of this and other alkali-metal coactivated SrS:Cu,F devices are summarized in
25 comparison to the non-coactivated SrS:Cu,F device in Table 2 below.

The EL luminance-voltage (L-V) and efficiency-voltage (-V) characteristics for a sodium-coactivated SrS:Cu,F device and a non-coactivated SrS:Cu,F device are shown in FIG.s 4 and 5 respectively. Upon coactivation, a dramatic increase in brightness and improvement in efficiency are evident. A summary of the
30 luminance (L40) and efficiency (E40) for each of the alkali metal coactivated SrS:Cu,F devices and the non-coactivated device is presented in Table 2. All

- 8 -

luminance and efficiency measurements were obtained 40 V above threshold at 60 Hz, using bipolar trapezoidal voltage pulses with 5 μ s rise and fall times and a width of 30 μ s.

5

TABLE 2

| Phosphor | L40 (cd/m ²) | E40 (lm/W) | CIE _x | CIE _y |
|--------------|--------------------------|------------|------------------|------------------|
| SrS:Cu,F | 9.57 | 0.136 | 0.164 | 0.268 |
| SrS:Cu, Li,F | 4.53 | 0.054 | 0.293 | 0.561 |
| SrS:Cu,Na,F | 45.8 | 0.819 | 0.317 | 0.585 |
| SrS:Cu,K,F | 52.7 | 0.973 | 0.289 | 0.596 |
| SrS:Cu,Rb,F | 30.6 | 0.193 | 0.285 | 0.577 |
| SrS:Cu,Cs,F | 21.6 | 0.138 | 0.291 | 0.577 |

- 10 The increased brightness and efficiency of the coactivated devices is partially due to improvements in phosphor crystallinity and diffuse reflectance. The improvement in crystallinity was confirmed by X-ray diffraction. The increased diffuse reflectance was deduced visually from the milky appearance of the coactivated phosphor when compared to the non-coactivated phosphor.
- 15 Improved crystallinity leads to more efficient electron transport and radioactive recombination in the phosphor and increased diffuse reflectance improves optical coupling.

- Coactivator treatment also leads to an improvement in the electrical characteristic of the ACTFEL devices. The internal charge-phosphor field ($Q-F_p$)
- 20 characteristics of a sodium coactivated SrS:Cu,F device and a non-coactivated SrS:Cu,F device are compared in FIG. 6. In comparison the coactivated device shows less charge being transported across the phosphor even though the

- 9 -

luminance of this device is greater. Less power is dissipated in the coactivated device as established by the smaller area enclosed by the $Q-F_p$ curve. The steady-state phosphor field of the green device is greater than that of the non-coactivated device and shows less overshoot. These last observations taken together imply
5 that the electric field is larger and more uniform across the phosphor for the coactivated device, leading to a greater luminance.

The preceding examples are set forth to illustrate the invention and are not intended to limit it. Additional embodiments and advantages within the scope of the claimed invention will be apparent to one of ordinary skill in the art. For
10 example, the phosphor materials can be used in devices other than ACTFEL devices.

- 10 -

We claim:

1. A phosphor material of the formula $Zn_{1-3x/2}M_xX:Mn$ wherein M is selected from the group consisting of the trivalent ions of Al, In, Ga, and mixtures thereof, and X is selected from the group consisting of S, Se, Te, and mixtures thereof.
2. A phosphor material of claim 1 wherein the emission maximum undergoes a systematic red shift as x is increased from 0.01 to 0.49.
3. A phosphor material of claim 1 wherein the amount of Mn is between 0.5 to 5.0 mol%.
4. A phosphor material of claim 1 wherein X is sulfur.
5. A luminescent device comprising a phosphor material of the formula $Zn_{1-3x/2}M_xX:Mn$ wherein M is selected from the group consisting of the trivalent ions of Al, In, Ga, and mixtures thereof, and X is selected from the group consisting of S, Se, Te, and mixtures thereof, where the emission maximum undergoes a systematic red shift as x is increased from 0.01 to 0.49.
6. A device of claim 5 wherein X is sulfur.
7. An alternating current thin-film electroluminescent device comprising:
a pair of dielectric layers suitable to substantially prevent DC current from flowing therebetween; and
a body of a phosphor material located between the dielectric layers, the phosphor material being of the formula $Zn_{1-3x/2}M_xX:Mn$ wherein M is selected from the group consisting of the trivalent ions of Al, In, Ga, and mixtures thereof, and X is selected from the group consisting of S, Se, Te, and mixtures thereof.

- 11 -

8. A phosphor material of the formula $MX:Cu, L, A$ wherein M is selected from the divalent ions of Sr, Mg, Ca, Ba, and mixtures thereof, X is selected from the group consisting of S, Se, Te, and mixtures thereof, L is selected from the group consisting of the trivalent cations of the lanthanides, Al, In, Ga, Sc, and mixtures thereof, and A is selected from the alkali metal ions and mixtures thereof.

9. A phosphor material of claim 8 wherein the emission maximum undergoes a systematic blue shift as the amount of L is increased from 0.05 to 5 mol% and undergoes a systematic red shift as the amount of A is increased from 0.05 to 5 mol%.

10. A phosphor material of claim 8 wherein the material contains 0.05 to 5.0 mol% copper.

15

11. A phosphor material of claim 8 wherein:
L is selected from the group consisting of the trivalent lanthanide cations and mixtures thereof; and
X is sulfur.

20

12. A phosphor material of claim 8 wherein the combined amount of L and A is equal to the amount of copper.

13. A luminescent device comprising a phosphor material of the formula, $MX:Cu, L, A$ wherein M is selected from the divalent ions of Sr, Mg, Ca, Ba, and mixtures thereof, X is selected from the group consisting of S, Se, Te, and mixtures thereof, L is selected from the group consisting of the trivalent cations of the lanthanides, Al, In, Ga, Sc, and mixtures thereof, and A is selected from the group consisting of the alkali metal ions and mixtures thereof, where the emission maximum undergoes a systematic blue shift as L is increased from 0.05 to 5 mol%

- 12 -

and undergoes a systematic red shift as A is increased from 0.05 to 5 mol%.

14. An alternating current thin-film electroluminescent device comprising:
a pair of dielectric layers suitable to substantially prevent DC current from
5 flowing therebetween; and
a body of a phosphor material located between the dielectric layers, the
phosphor material being of the formula $MX:Cu, L, A$ wherein M is selected from
the divalent ions of Sr, Mg, Ca, Ba, and mixtures thereof, X is selected from the
group consisting of S, Se, Te, and mixtures thereof, L is selected from the group
10 consisting of the trivalent cations of the lanthanides, Al, In, Ga, Sc, and mixtures
thereof, and A is selected from the alkali metal ions and mixtures thereof.

15. A luminescent device comprising:
at least one phosphor material selected from the group consisting of a
15 phosphor of the formula $Zn_{1-3x/2}M_xX:Mn$ wherein M is selected from the group
consisting of the trivalent ions of Al, In, Ga, and mixtures thereof, and X is
selected from the group consisting of S, Se, Te, and mixtures thereof, where the
emission maximum undergoes a red shift as x increases from 0.01 to 0.49; and
at least one phosphor material of the formula, $MX:Cu, L, A$ wherein M
20 is selected from the divalent ions of Sr, Mg, Ca, Ba, and mixtures thereof, X is
selected from the group consisting of S, Se, Te, and mixtures thereof, L is
selected from the group consisting of the trivalent cations of the lanthanides, Al,
In, Ga, Sc, and mixtures thereof, and A is selected from the group consisting of
the alkali metal ions and mixtures thereof, where the emission maximum
25 undergoes a systematic blue shift as the amount of L is increased from 0.05 to 5
mol% and undergoes a systematic red shift as A is increased from 0.05 to 5
mol%.

- 13 -

16. The luminescent device of claim 15 wherein:

L is selected from the group consisting of the trivalent lanthanide cations and mixtures thereof; and

X is sulfur.

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17. An alternating current thin-film electroluminescent device comprising:

a pair of dielectric layers suitable to substantially prevent DC current from flowing therebetween; and

a body of a phosphor material located between the dielectric layers, the
10 phosphor material comprising (a) at least one phosphor material selected from the group consisting of a phosphor of the formula $Zn_{1-3x/2}M_xX:Mn$ wherein M is selected from the group consisting of the trivalent ions of Al, In, Ga, and mixtures thereof, and X is selected from the group consisting of S, Se, Te, and mixtures thereof and (b) at least one phosphor material of the formula $MX:Cu, L, A$
15 wherein M is selected from the divalent ions of Sr, Mg, Ca, Ba, and mixtures thereof, X is selected from the group consisting of S, Se, Te, and mixtures thereof, L is selected from the group consisting of the trivalent cations of the lanthanides, Al, In, Ga, Sc, and mixtures thereof, and A is selected from the group consisting of the alkali metal ions and mixtures thereof.

20

18. The method of providing a luminescent device, the method comprising:

providing a substrate; and

applying to the substrate at least one phosphor material selected from the
25 group consisting of (a) phosphor materials of the formula $Zn_{1-3x/2}M_xX:Mn$ wherein M is selected from the group consisting of the trivalent ions of Al, In, Ga, and mixtures thereof, and X is selected from the group consisting of S, Se, Te, and mixtures thereof and (b) phosphor materials of the formula $MX:Cu, L, A$ wherein M is selected from the divalent ions of Sr, Mg, Ca, Ba, and mixtures thereof, X is
30 selected from the group consisting of S, Se, Te, and mixtures thereof, L is selected from the group consisting of the trivalent cations of the lanthanides, Al,

- 14 -

In, Ga, Sc, and mixtures thereof, and A is selected from the alkali metal ions and mixtures thereof.

19. A method of producing a phosphor composition that exhibits a luminescence spectrum with a target wavelength maximum, comprising:

- 5 a) providing a first codoped alkaline earth chalcogenide phosphor composition of the formula $MX:Cu, L, A$ wherein M is selected from the divalent ions of Sr, Mg, Ca, Ba, and mixtures thereof, X is selected from the group consisting of S, Se, Te, and mixtures thereof, L is selected from the group consisting of the trivalent cations of the lanthanides, Al, In, Ga, Sc, and mixtures thereof, and A is selected from the group consisting of the alkali metal ions and mixtures thereof;
- 10 b) measuring a luminescence spectrum of a sample of the first phosphor composition;
- 15 c) determining if the first phosphor composition has a wavelength of maximum luminescence greater or less than the target wavelength;
- 20 d) preparing a sample of a second phosphor composition with an adjusted amount of L relative to the amount of A wherein the amount of L is increased relative to the amount of A as compared to the first phosphor composition if the luminescence spectrum of the first phosphor composition exhibits a wavelength of maximum luminescence greater than the target wavelength maximum and the amount of L is decreased relative to the amount of A as compared to the first phosphor composition if luminescence spectrum of the first phosphor composition exhibits a wavelength of maximum luminescence less than the target wavelength maximum; and
- 25 e) repeating steps b through d until a phosphor composition exhibiting a wavelength of maximum luminescence that matches the target wavelength is prepared.

30 20. The method of claim 19 wherein the combined amount of L and A is held constant.

- 15 -

21. The method of claim 20 wherein the aggregate amount of L and A is equal to the amount of copper codopant.

22. A method of producing a phosphor that will exhibit a luminescence spectrum with a target maximum wavelength, comprising:

5 a) preparing a plurality of phosphor compositions of the formula $MX:Cu$, L, A wherein the identity of M and X are fixed, the combined amount of L and A is held constant, the ratio of L and A is varied, the amount of copper is held constant, M is selected from the divalent ions of Sr, Mg, Ca, Ba, and mixtures thereof, X is selected from the group consisting of S, Se, Te, and mixtures thereof, L is selected from the group consisting of the trivalent cations of the lanthanides, Al, In, Ga, Sc, and mixtures thereof, and A is selected from the group consisting of the alkali metal ions and mixtures thereof;

10 measuring the wavelength of maximum luminescence for each member of the plurality of phosphor samples;

preparing a calibration curve which relates the ratio of L to A to the wavelength of maximum luminescence;

determining from the calibration curve the ratio of L to A predicted to achieve the target wavelength maximum; and

20 preparing a phosphor of the predicted composition.

23. A method of producing a phosphor composition that exhibits a luminescence spectrum with a target wavelength maximum, comprising:

25 a) providing a first codoped zinc chalcogenide phosphor of the formula, $Zn_{1-3x/2}M_xX:Mn$, wherein M is selected from the group consisting of the trivalent ions of Al, In, Ga, and mixtures thereof, and X is selected from the group consisting of S, Se, Te, and mixtures thereof;

b) measuring a luminescence spectrum of a sample of the first phosphor composition conforming to the formula $Zn_{1-3x/2}M_xX:Mn$;

30 c) determining if the first phosphor composition has a wavelength of maximum luminescence greater or less than the target wavelength;

- 16 -

d) preparing a sample of a second phosphor composition with an adjusted amount of M as compared to the first phosphor composition wherein the amount of M is decreased if the luminescence spectrum of the first phosphor composition exhibits a wavelength of maximum luminescence greater than the target wavelength maximum and the amount of M is decreased as compared to the first phosphor composition if the luminescence spectrum of the first phosphor composition exhibits a wavelength of maximum luminescence less than the target wavelength maximum; and

e) repeating steps b through d until a phosphor composition exhibiting a wavelength of maximum luminescence that matches the target wavelength is prepared.

24. A method of producing a phosphor compositions that exhibits a luminescence spectrum with a target wavelength maximum, comprising:

preparing a plurality of phosphor samples of the formula $Zn_{1-3x/2}M_xX:Mn$ wherein the identity of M and X are fixed, the ratio of M to Zn varies, the amount of manganese is held constant, M is selected from the group consisting of the trivalent ions of Al, In, Ga, and mixtures thereof, and X is selected from the group consisting of S, Se, Te, and mixtures thereof;

measuring the wavelength of maximum luminescence for each member of the plurality of phosphor samples;

preparing a calibration curve which relates the ratio of M to Zn to the wavelength of maximum luminescence;

determining from the calibration curve the ratio of M to Zn predicted to achieve the target wavelength maximum; and

preparing a phosphor of the predicted composition.

1/5

FIG. 1

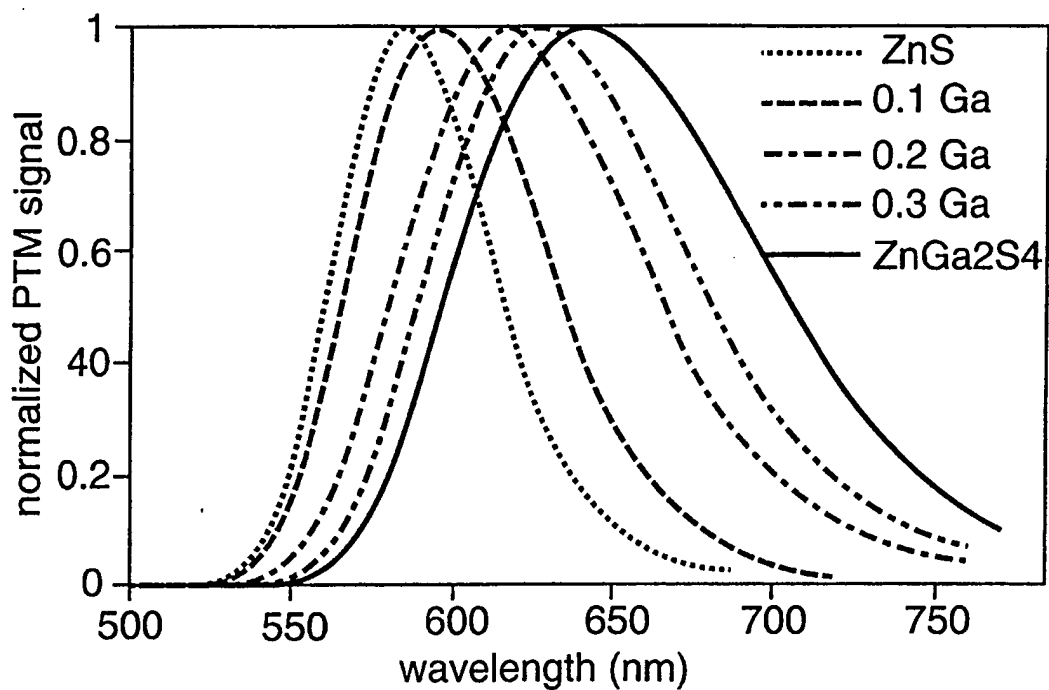
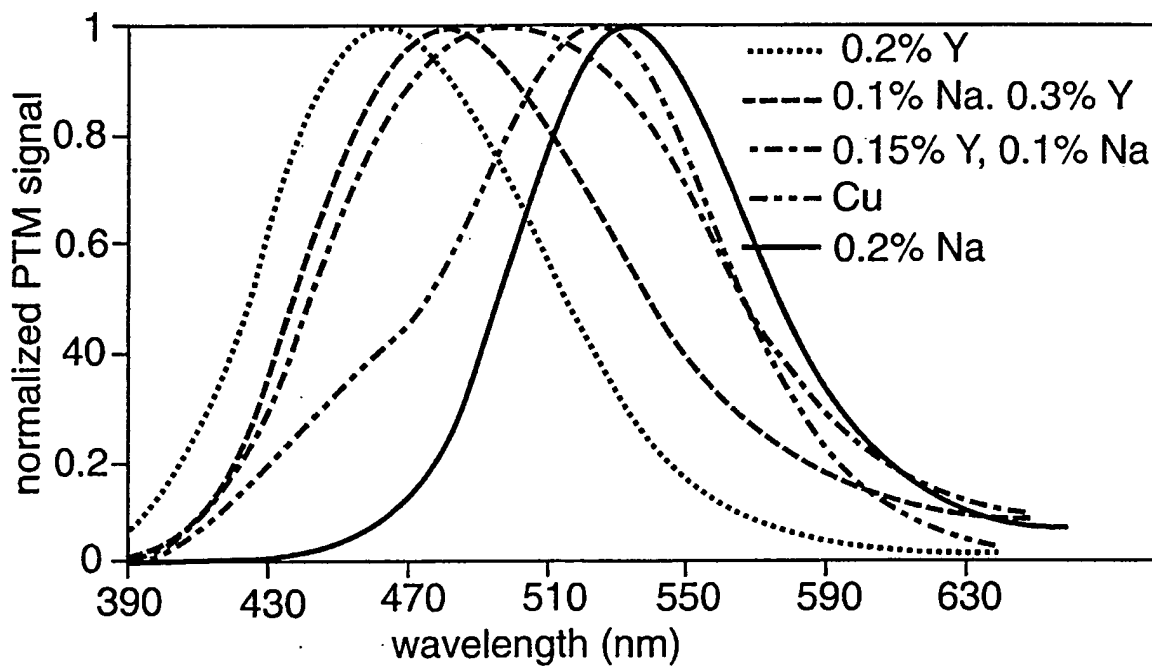


FIG. 2



2/5

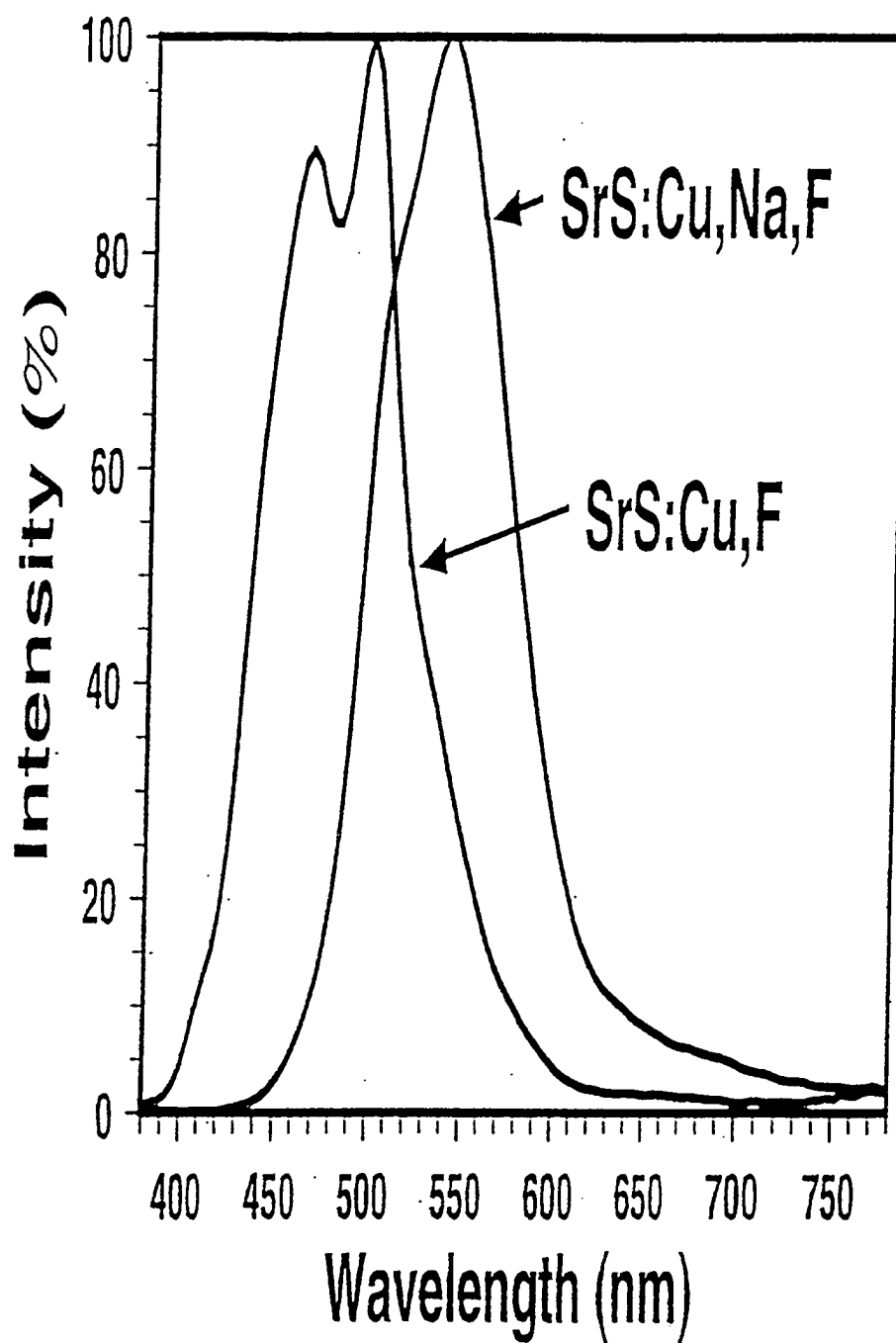


FIG. 3

3/5

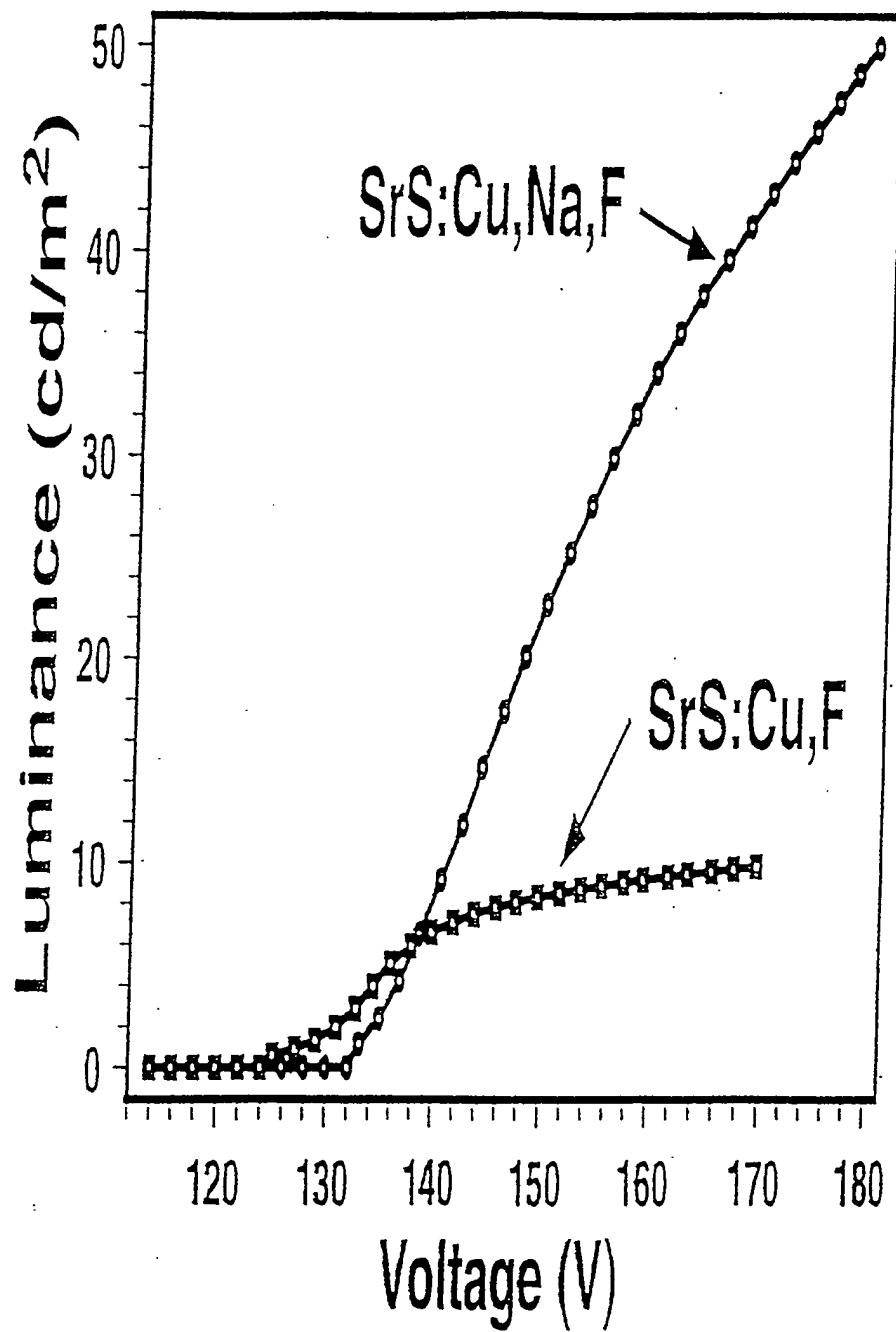


FIG. 4

4/5

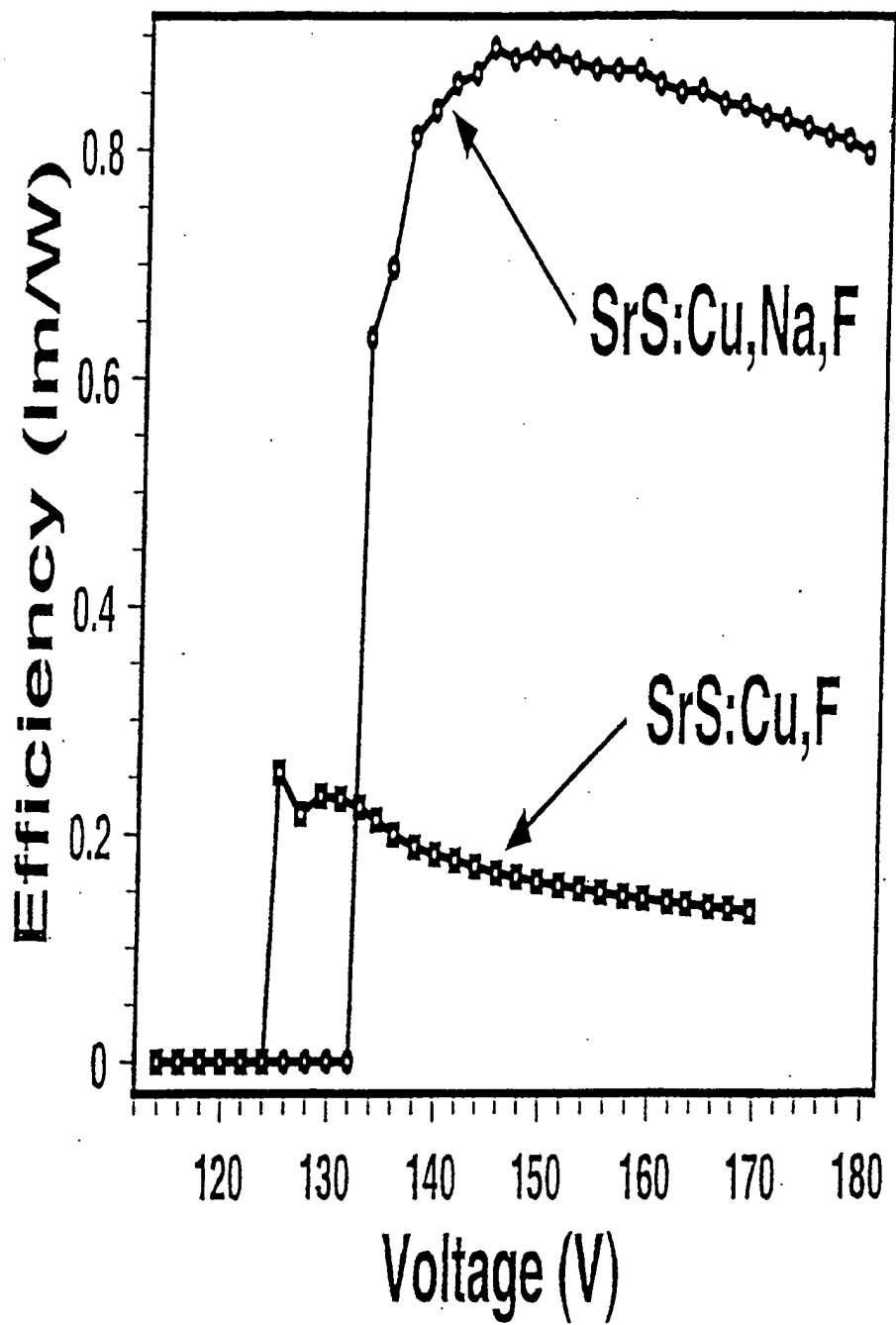


FIG. 5

5/5

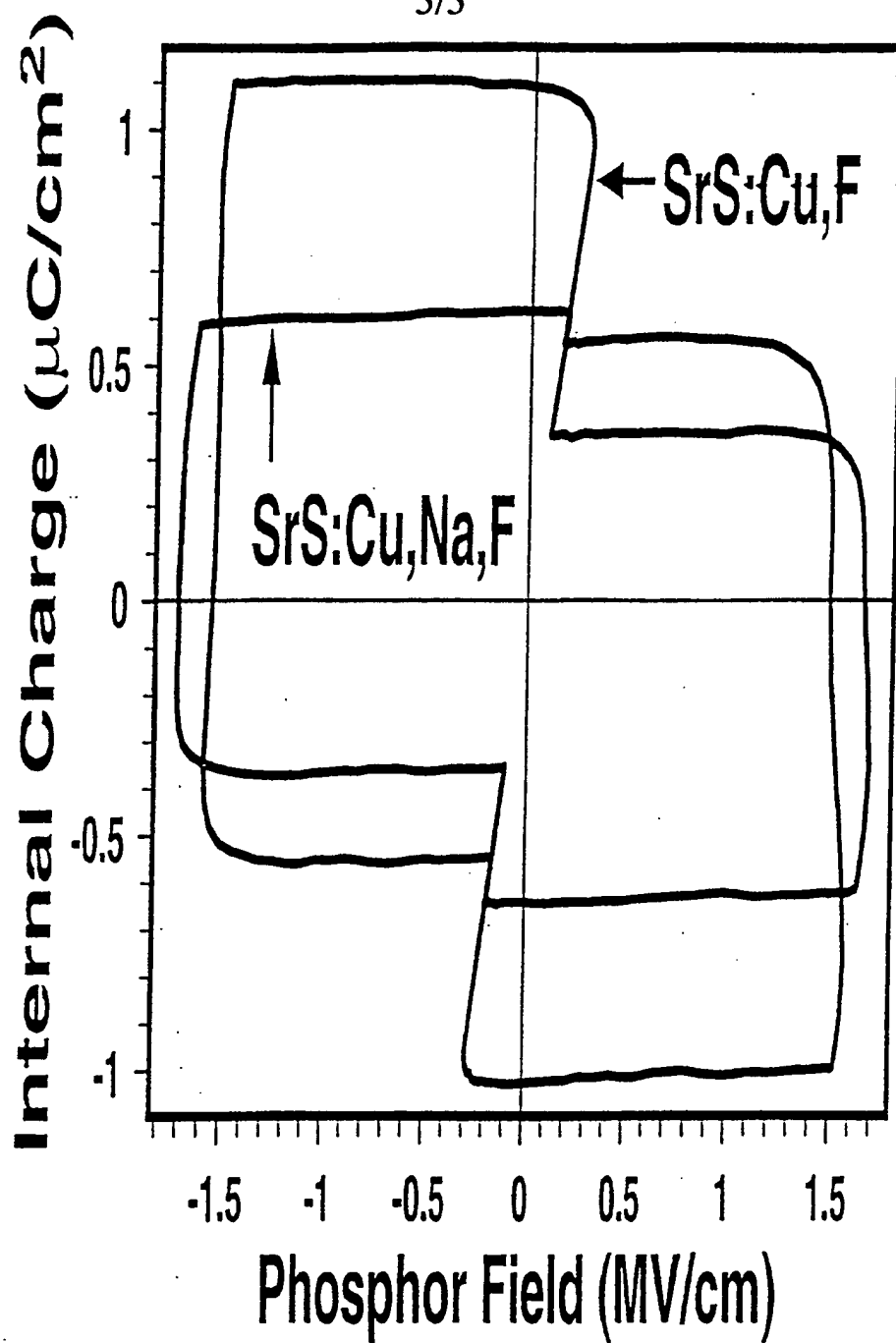


FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/21578

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C09K 11/08; H05B 33/00, 33/18

US CL :Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/301.4R, 301.4S; 257/101, 102, 103; 427/64, 66; 428/690, 917; 313/503, 509; 423/508, 511

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------------|--|--|
| X ----- Y | JP 8-88086 A (NIPPON DENSO CO) 02 April 1996 (02.04.96), the whole document, especially the abstract and Figures 1 and 4. | 1, 4, 7, 18 ----- 2, 3, 5, 6, 15-17, 23, 24 |
| X ----- Y | GB 2 319 777 A (PLANAR SYSTEMS INC) 03 June 1998 (03.06.98), the whole document, especially the abstract, page 2, line 28 to p. 3, l. 22, p. 4, l. 6-32, and p. 6, l. 37 to p. 7, l. 33. | 1, 4, 7, 8, 10-12, 14, 17, 18 ----- 2, 3, 5, 6, 9, 13, 15, 16, 19-24 |



Further documents are listed in the continuation of Box C.



See patent family annex.

| | |
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| * Special categories of cited documents: | *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention |
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| *O* document referring to an oral disclosure, use, exhibition or other means | |
| *P* document published prior to the international filing date but later than the priority date claimed | |

Date of the actual completion of the international search

29 NOVEMBER 1999

Date of mailing of the international search report

14 DEC 1999

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Commissioner of Patents and Trademarks
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Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

MARIE R. YAMNITZKY

Telephone No. (703) 308-0651

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/21578

| C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT | | |
|---|--|--|
| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| X ----- Y | US 4,725,344 A (YOCOM et al) 16 February 1988 (16.02.88), the whole document, especially column 2, line 54 to c. 3, l. 13, c. 4, l. 23-51, and the Examples. | 8, 10-12, 14, 18 ----- 9, 13, 15-17, 19-22 |
| X ----- Y | JP 60-147490 A (YOSHIDA) 03 August 1985 (03.08.85), the whole document, especially the abstract and Tables 2, 3 and 5 (pages 587 and 589). | 8-14, 18 ----- 15-17, 19-22 |
| X ----- Y | EP 0 057 610 A2 (HITACHI, LTD) 11 August 1982 (11.08.82), the abstract, page 3, line 9 to p. 6, l. 17, p. 13, l. 6 to p. 19, l. 10. | 8-14, 18 ----- 15-17, 19-22 |
| Y | US 4,374,037 A (TAKAHASHI) 15 February 1983 (15.02.83), the whole document, especially column 3, line 20 to c. 4, l. 53, and c. 5, l. 5-7. | 8-22 |

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JS99/21578

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

252/301.4R, 301.4S; 257/101, 102, 103; 427/64, 66; 428/690; 313/503, 509

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

STN/REGISTRY, HCA

search terms: zn, al, in, ga, s, se, te, mn, manganese#, sr, mg, ca, ba, cu, copper#, lnth, la, sc, sodium#, na, potassium#, k, lithium#, li, rubidium#, rb, coactiv?, phosphor#, phosphores?, actfel#, electrolumin?, electro (2a) lumin?, el, e (w) l. led, light? (3a) (emiss? or emit?) (3a) diod?, ?lumine?, metal#####, elemental?, atom?, dope#, doping#, dopant?, pure#, purif?, ion#, cation##, lanthanid?, lanthanon?